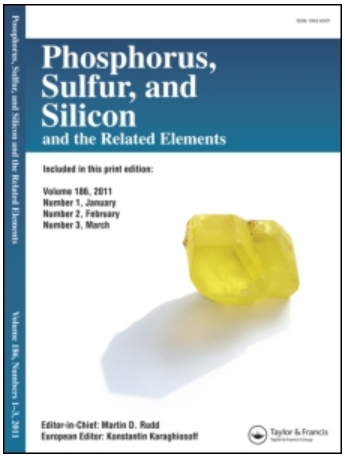

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SYNTHESIS OF NOVEL TRITHIOCARBONATE-*S*-OXIDES

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The oxidation of the trithiocarbonates ***3*** *with* m-*chloroperoxybenzoic acid* (m-*CPBA) in chloroform at room temperature provides an efficient stereoselective synthesis of the* (E) *sulfine* $\mathbf{4_a}$ *and* (Z) *sulfine* $\mathbf{4_b}$*. The expected* (E) *and* (Z) *configurations of* $\mathbf{4_{a,b}}$ *were confirmed by x-ray structure determination. The Sulfines* ***4*** *were further structurally elucidated by their cycloaddition reactions with 2,3-dimethyl-1,3-butadiene in chloroform at room temperature to give the corresponding dihydrothiopyran* S-*oxides* $\mathbf{5_{a,b}}$ *in a quantitative yield.*

Keywords: Chlorodithioformates; dihydrothiopyran-*S*-oxide; oxidation; sulfines; trithiocarbonate

Sulfines **1** are important heterocumulenes with a >C═S═O moiety. Extensive studies of these thiocarbonyl oxides were carried out by the group of B. Zwanenburg[1–4] in the 1970s. In spite of recent studies by other groups,[5–25] sulfine chemistry, in particularly the synthetic applications of sulfine, has yet to be fully exploited.

Sulfines are synthesized via several synthetic pathways. The most two versatile routes to these sulfur-centered heterocumulenes are the oxidation of thiocarbonyl-containing compounds with peracids, and the alkylidenation of sulfur dioxide by means of α-silyl carbanions.[3,4]

The purpose of the work presented in this article is to extend the chemistry of chlorodithioformates **2**. Another intriguing point to be addressed is the question of the relative reactivities of the >C═S double bonds of the starting **2** and the corresponding sulfine **4**. The present work also quantifies the steric demands of the R^1S and R^2S groups

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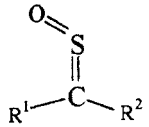
of **3** and their competition for the *E*- and *Z*-positions in the resulted sulfines **4**, and examines the selective oxidation of trithiocarbonates, a compound which contains three oxidizable sulfur atoms.

RESULTS AND DISCUSSIONS

The starting unsymmetrical diaryltrithiocarbonates **3** were prepared by the reaction of arylchlorodithioformates **2** with *p*-chlorothiophenol in the presence of NaOH according to (1) in 90% yields.



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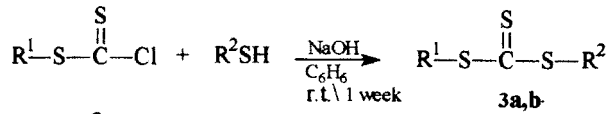


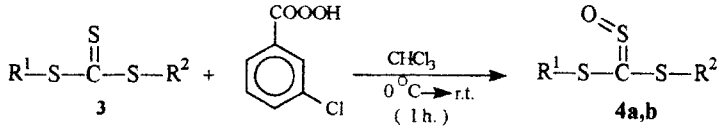
2 **3a,b** (1)

a: $R^1 = C_6H_5$, $R^2 = 4\text{-}ClC_6H_4$

b: $R^1 = C_6Cl_5$, $R^2 = 4\text{-}ClC_6H_4$

The ^{13}C NMR signal of the >C=S group of **3** resonates at 224 ppm for **3a** and at 216.53 ppm for **3b** lower field shift compared with the starting chlorodithioformates **1** which resonate at 198.10 for **1a** and 189.50 ppm for **1b** respectively.

The oxidation of trithiocarbonates **3** with *m*-chloroperbenzoic acid (*m*-CPBA) at 0°C in chloroform for 1 h affords the corresponding sulfines **4** in quantitative yields with a high chemoselectivity according to (2). The crude material of the yellow sulfines **4** was analyzed by NMR which showed that the oxidation of the thiocarbonyl group was stereo selective and mainly a single isomer was formed. No evidence for the oxidation of the other sulfur atoms of **3** was detected when the crude material was



3 **4a,b** (2)

a: $R^1 = C_6H_5$, $R^2 = 4\text{-}ClC_6H_4$

b: $R^1 = C_6Cl_5$, $R^2 = 4\text{-}ClC_6H_4$

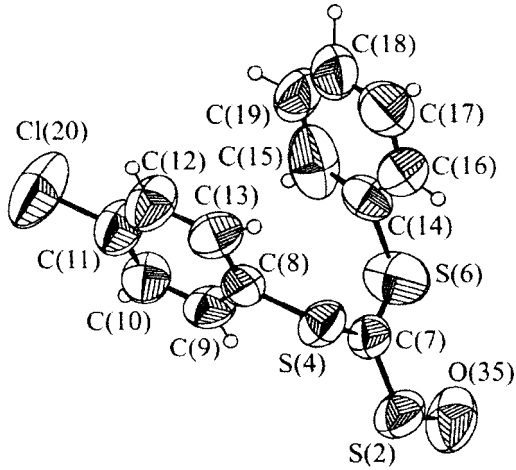


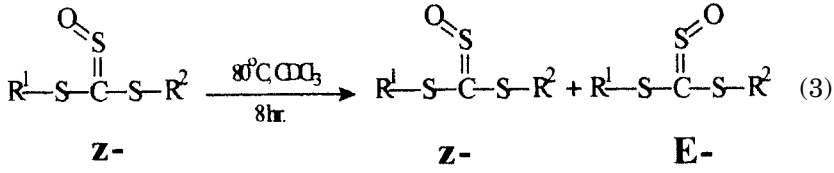
FIGURE 1 The molecular structure of sulfine **4a** with 50% probability ellipsoids. Crystal system: orthorhombic, space group: *P* n a 21, unit cell dimensions (Å): $a = 26.1600$, $b = 6.9700$, $c = 15.3300$, Cell volume: 2795.2 (Å^3), $R_{All} = 0.068$. Selected geometric parameters (Å): S2–O35 = 1.45, S2–C7 = 1.632, S4–C7 = 1.734, S4–C8 = 1.735, S6–C7 = 1.720, S6–C14 = 1.776; C8–S4–C7 = 104.99, C7–S2–O35 = 110.93, S2–C7–S6 = 113.04, C7–S6–C14 = 103.71, S4–C7–S6 = 128.16, S2–C7–S4 = 117.76.

carefully inspected by the NMR. It should be noted that the *E*-sulfine isomer is predominantly obtained in case of sulfine **4a** according to x-ray structure determination (Figure 1) which reveals that oxygen delivery occurs opposite to the more bulky aryl group, where as in case of sulfine **4b** the oxygen atom located cis to the bulky pentachlorophenyl group. Namely it prefers *Z*-geometry according to x-ray structure determination (Figure 3).

The quaternary (>C=S=O) carbon of the sulfines **4** exhibited an up field shift of 187.00 ppm for **4a** and 181.00 ppm for **4b**, respectively, in ^{13}C NMR, up field from the corresponding (>C=S) group of the starting thiocarbonyl compounds **3** (224.00 ppm for **3a** and 216.53 ppm for **3b**) respectively. This shift was found to be within the range reported for other sulfines (176–196 ppm).

Moreover, the strong IR absorption at 1110 and 1088 cm^{-1} for **4a**, and at 1115 and 1095 cm^{-1} for **4b** can be attributed to the (>C=S=O) group for the corresponding sulfines **4a** and **4b** respectively. It should be noted that the sulfines **4** can be kept without alteration for months at ambient temperature in contrast to other reported sulfines.[1] Also **4** can be purified by column chromatography on silica gel or by crystallization. The stability of *Z*-sulfine **4b** is not configurationally stable in $CDCl_3$

solution at 80°C. Because of isomerization to (*E*) and (*Z*) mixtures after 8 hours in (1:1) ratio according to (3), while sulfine **4a** remains stable (unchanged). Thus (*E*) and (*Z*) isomers of **4b** have relatively close thermodynamic stabilities. The isomerization mechanism is not yet clear and is not observed with sulfines derived from thioketones[26] or thionoesters.[27]



(3)

$R^1 = C_6Cl_5$; $R^2 = 4\text{-}ClC_6H_4$

This observation revealed that the kinetic isomer is not the one which has the oxygen atom on the less hindered side of the >C=S double bond, (i.e. The kinetic oxidation has taken place on the more hindered position of the thiocarbonyl sulfur). While the thermodynamically stable isomer is the one which has the oxygen on the opposite side of the bulky group.

The non-linearity of the >C=S=O system of **4a** was established by a single crystal x-ray structure* determination (Figure 1). The >C=S and S=O bonds were found to be 1.632 and 1.45 Å, respectively, while the >C=S=O angle was found to be 110.93°. The sulfine exhibits a nonplanar arrangement with the oxygen atom located trans to the *p*-chlorophenyl group. The dihedral angle between the planes of the sulfine group and the *p*-chlorophenylthio group is 103.71°, demonstrating a nonplanar arrangement around the C(7)–S(6) bond. The sulfine moiety π-plane and the *p*-chlorophenylthio group are arranged perpendicular to each other, where the bulky parachlorophenylthio group hinders the sulfine moiety to adopt a position in the same plane as the *p*-chlorophenyl ring.

Also, the non-linearity of the >C=S=O system of **4a**\ was established by a single crystal x-ray structure* determination (Figure 2). The >C=S and S=O bonds were found to be 1.618 and 1.483 Å, respectively, while the >C=S=O angle was found to be 111.59°. The sulfine exhibits a nonplanar arrangement with the oxygen atom located trans to the *p*-chlorophenyl group. The dihedral angle between the planes of the sulfine group and the *p*-chlorophenyl group is 102.99°, demonstrating a nonplanar arrangement around the C(34)–S(5) bond. The sulfine

*The crystallographic data has been deposited at the Cambridge Crystallographic Data Center, U.K.

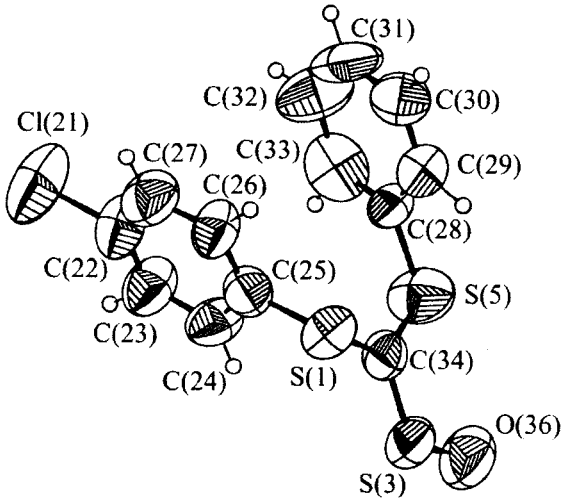
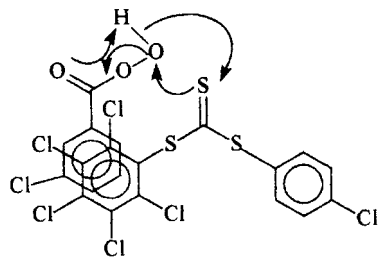


FIGURE 2 The molecular structure of sulfine **4a** with 50% probability ellipsoids. Crystal system: orthorhombic, space group: *P* n a 21, unit cell dimensions (Å): $a = 26.1600$, $b = 6.9700$, $c = 15.3300$, Cell volume: 2795.2 (Å), $R_{All} = 0.068$. Selected geometric parameters (Å): S3–O36 = 1.483, S3–C34 = 1.618, S5–C34 = 1.704, S5–C28 = 1.784, S1–C34 = 1.719, S1–C25 = 1.775; C34–S3–O36 = 111.59, S1–C34–S3 = 113.25, C25–S1–C34 = 102.99, S1–C34–S5 = 118.29, C28–S5–C34 = 104.17, S5–C34–S3 = 128.71.

moiety π-plane and the *p*-chlorophenylthio group are arranged perpendicular to each other, where the bulky chlorophenyl group hinders the sulfine moiety to adopt a position in the same plane as the *p*-chlorophenyl ring. This may explain that the oxygen atom was introduced to the more hindered side of the >C=S double bond, namely that of pentachlorophenylthio group. This might be a new example of π-stacking, taking place between the pentachlorophenyl nuclei of the trithiocarbonate and the electrophilic (*m*-CPBA) as shown in the structure below.



(*m*-CPBA)

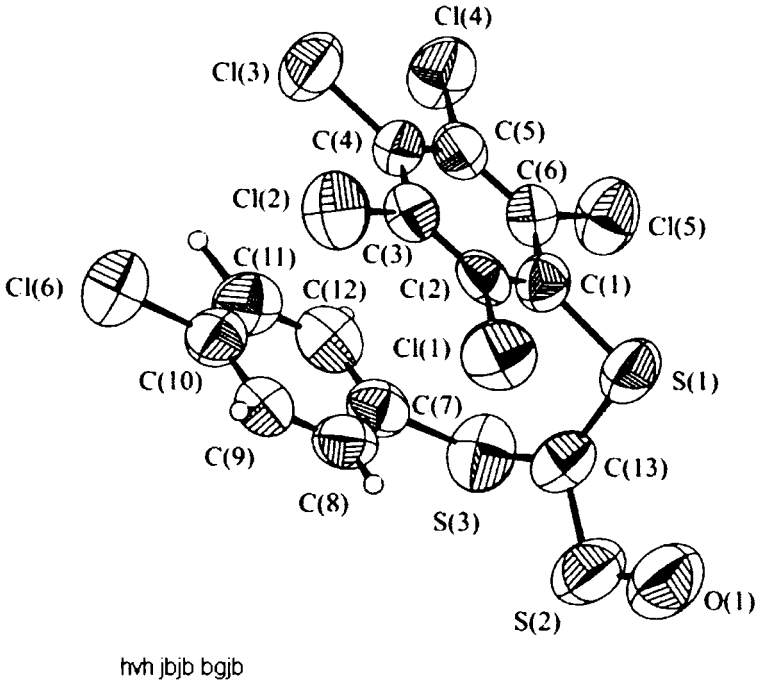
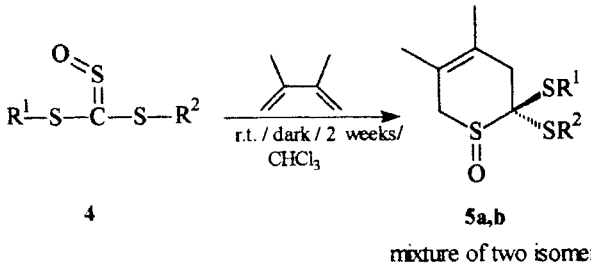


FIGURE 3 The molecular structure of sulfine **4b** with 50% probability ellipsoids. Crystal system: monoclinic, space group: *P* 1 21/n 1, unit cell dimensions (Å): $a = 10.614$, $b = 12.995$, $c = 13.381$, $\square = 112.14^\circ$, Cell volume: 1709.54, $R_{All} = 0.086$. Selected geometric parameters (Å): S1–C13 = 1.738, S1–C1 = 1.761, S3–C13 = 1.752, S3–C7 = 1.777, S2–O1 = 1.467, S2–C13 = 1.642, C13–S1–C1 = 99.72, C13–S3–C7 = 103.34, O1–S2–C13 = 113.88, S2–C13–S1 = 119.57, S2–C13–S3 = 112.32, S1–C13–S3 = 127.14.

The nonlinearity of the >C=S=O system of **4b** was established by a single crystal x-ray structure determination (Figure 3). The >C=S and S=O bonds were found to be 1.642 and 1.467 Å, respectively, while the >C=S=O angle was found to be 113.88°. The sulfine exhibits a non-planar arrangement with the oxygen atom located *cis* to the pentachlorophenyl group. The dihedral angle between the planes of the sulfine group and the pentachlorophenyl group is 99.72°, demonstrating a nonplanar arrangement around the C(13)–S(1) bond. The sulfine moiety π-plane and the pentachlorophenylthio group are arranged perpendicular to each other, where the bulky group hinders the sulfine moiety to adopt a position in the same plane as the *p*-chlorophenyl ring.

The sulfines **4** were further structurally elucidated by their cycloaddition reactions with 2,3-dimethyl-1,3-butadiene in chloroform at room

temperature. The corresponding Diels-Alder adducts **5** were formed in nearly quantitative yield according to (4) with the formation of two isomers as concluded from the NMR spectra of the crude product.



4 **5a,b**

mixture of two isomers

(4)

A ^{13}C NMR signal of the thiocarbonyl carbon of **4** shifted to a higher field and became tertiary in the corresponding adducts **5** and splits into two signals owing to the nonplanarity of the sulfoxide moiety in dihydrothiopyran-*S*-oxides **5**. An attempt to isolate both isomers has been failed due to spontaneous decomposition on silica gel.

EXPERIMENTAL

All ^1H and ^{13}C NMR experiments (solvent $CDCl_3$) were carried out with a Varian Unity 400 MHz spectrometer (400 MHz for ^1H, 100 MHz for ^{13}C) in Uppsala University, Sweden. Chemical shifts were expressed as δ in parts per million (ppm) relative to the respective solvent. Mass spectroscopy was measured on a Kratos 50 tc spectrometer, and melting points were recorded on a Büchi melting point apparatus and are uncorrected. TLC was done on Merck Kiesel gel F_{254} precoated plates (Merck), column chromatography was carried out using silica gel (0.040–0.063 mm) from Merck, and the microanalysis performed in the microanalysis lab at (Cairo University). Single crystals suitable for x-ray studies from sulfines **4a**,**b** were obtained by slow crystallization from hexane. Aryl chlorodithioformates[28] and aryl trithiocarbonates[29] were prepared according to literature procedures.

p-Chlorophenyl(phenyl)trithiocarbonate 3a

The *p*-chlorothiophenol (306 mg, 2.10 mmol) in benzene (10 ml) was added to a solution of sodium hydroxide (84 mg, 0.20 mmol) in water (8 ml) at room temperature. After stirring for 2 h, phenylchlorodithioformate (400 mg, 2.10 mmol) was then added dropwise to the above mixture at room temperature over a period of 30 min, the reaction mixture

was kept for 7 days. The benzene solution was washed successively with three times water. The organic layer was dried over anhydrous $CaCl_2$, filtrated and then concentrated under reduced pressure to leave an oily substance, which was treated with *n*-hexane to give a yellow solid. The solid product crystallized from *n*-hexane, in 92% yield as yellow crystals; m.p. 80–82°C. IR (KBr) cm^{-1}: 1565, 1470, 1453, 1385, 1095 ($\nu_{C=S}$), 854, 745, 685; ^1H NMR ($CDCl_3$-d_6) ppm: 7.44 (s, 2H), 7.49–7.52 (m, 3H), 7.54–7.56 (m, 4H); ^{13}C NMR ($CDCl_3$-d_6) ppm: 128.92, 129.60, 129.83, 130.30, 130.87, 135.55, 136.83, 137.28, 224.03 (C=S); MS: *m*/*z* (%) 296 (22, M, $C_{13}H_9ClS_3$), 219 (1, $C_7H_4ClS_3$), 187 (35, $C_7H_4ClS_2$), 153 (100, $C_7H_5S_2$), 111 (27, C_6H_4Cl), 77 (42, C_6H_5); Anal. Calcd for $C_{13}H_9ClS_3$ (296.50): C, 52.61; H, 3.03; S, 32.37. Found: C, 52.60; H, 3.32; S, 32.05%.

p-Chlorophenyl(pentachlorophenyl)trithiocarbonate 3b

The *p*-chlorothiophenol (158 mg, 1.10 mmol) in benzene (10 ml) and a solution of sodium hydroxide (44 mg, 1.10 mmol) in water (4 ml) was added at room temperature. After stirring for 2 h, pentachlorophenyl chlorodithioformate (400 mg, 1.10 mmol) was then added dropwise to the above mixture at room temperature over a period of 30 min, the reaction mixture was stirred for 7 days at room temperature. The benzene solution was washed successively three times with water. The organic layer was dried over anhydrous $CaCl_2$, filtrated and then concentrated under reduced pressure to leave a yellow solid. The product was recrystallized from *n*-hexane, in 89% yield as yellow crystals; m.p. 93–96°C. IR (KBr) cm^{-1}: 1345, 1305, 1095, 1082 ($\nu_{C=S}$), 1015, 880, 692; ^1H NMR ($CDCl_3$-d_6) ppm: 7.48–7.55 (m, 4H); ^{13}C NMR ($CDCl_3$-d_6) ppm: 128.60, 130.48, 131.12, 133.11, 137.09, 137.48, 138.29, 139.21, 216.53 (C=S); MS: *m*/*z* (%) 326, $C_{13}H_4Cl_2S_3$), 247 (12, C_6C_{15}), 219 (1, $C_7H_4ClS_3$), 187 (100, $C_7H_4ClS_2$), 143 (24, C_6H_4ClS), 111 (72, C_6H_4Cl), 76 (6, C_6H_4); Anal. Calcd. for $C_{13}H_4Cl_6S_3$ (469): C, 33.26; H, 0.85; S, 20.47. Found: C, 33.24; H, 0.89; S, 20.42%.

p-Chlorophenylthio(phenylthio)sulfine 4a

To a stirred solution of **3a** (300 mg, 1.01 mmol) in chloroform (5 ml) at 0°C, a single portion of *m*-chloroperbenzoic acid (75%, 230 mg, 1.33 mmol) was added. The mixture was stirred at 0°C for 1 h. The chloroform solution was washed successively with saturated aqueous sodium hydrogen carbonate three times. The organic layer was dried over anhydrous $CaCl_2$, filtrated and then concentrated under reduced pressure to leave an oily substance, which was dissolved in diethyl ether (3 ml) and cooled overnight to give a yellow solid. The solid

product crystallized from *n*-hexane, in 84% yield as yellow crystals; m.p. 83–85°C. IR (KBr) cm^{-1}: 1470, 1390, 1110, 1088, 1110 ($\nu_{C=S=O}$), 815, 750, 690; ^1H NMR ($CDCl_3$-d_6) ppm: 6.96–6.99 (m, 2H), 7.20–7.33 (m, 4H), 7.41–7.45 (m, 2H), 7.37–7.42 (m, 1H); ^{13}C NMR ($CDCl_3$-d_6) ppm: 129.03, 129.27, 130.03, 130.21, 131.16, 134.82, 135.63, 136.77, 187.11 (>C=S=O); MS: *m*/*z* (%): 312 (29, M, $C_{13}H_9ClOS_3$), 235 (1, $C_7H_4ClOS_3$), 55 (57, C_7H_4ClS), 121 (62, C_7H_5S), 109 (100, C_6H_5S), 77 (66, C_6H_5); Anal. Calcd. For $C_{13}H_9ClOS_3$ (312.52): C, 49.92; H, 2.88; S, 30.72. Found: C, 49.62; H, 2.60; S, 30.58%.

p-Chlorophenylthio(pentachlorophenylthio)sulfine 4b

To a stirred solution of **3b** (100 mg, 2.10 mmol) in chloroform (5 ml) at 0°C, *m*-chloroperbenzoic acid (75%, 49 mg, 2.80 mmol) was added as a single portion. The mixture was stirred at 0°C for 1 h. The chloroform solution was washed successively with saturated sodium hydrogen carbonate solution three times.The organic layer was dried over anhydrous $CaCl_2$, filtrated, and then concentrated under reduced pressure to leave a yellow solid. The solid product crystallized from CH_2Cl_2/*n*-hexane (1:3), in 80% yield as yellow crystals; m.p. 86–89°C. IR (KBr) cm^{-1}: 1480, 1332, 1300, 1115, 1095 ($\nu_{C=S=O}$), 820, 685; ^1H NMR ($CDCl_3$-d_6) ppm: 7.02–7.05 (m, 2H), 7.24–7.25 (m, 2H); ^{13}C NMR ($CDCl_3$-d_6) ppm: 128.69, 129.57, 129.74, 130.86, 131.80, 132.46, 136.00, 138.77, 180.99 (C=S=O); MS: *m*/*z* (%) 447 (4, $C_{13}H_4Cl_5OS_3$), 323 (4, $C_7Cl_5S_2$), 279 (26, C_6Cl_5S), 219 (27, $C_7H_4ClS_3$), 203 (2, $C_7H_4ClOS_2$), 187 (64, $C_7H_4ClS_2$), 143 (100, C_6H_4ClS), 111 (63, C_6H_4Cl). Anal. Calcd. for $C_{13}H_4Cl_6OS_3$ (485): C, 32.16; H, 0.82; S, 19.79. Found: C, 32.40; H, 1.00; S, 19.56%.

5,6-Dihydro-3,4-dimethyl-6-(*p*-chlorophenylthio)-6-(phenylthio)-2H-thiopyran-*S*-oxide 5a

A large excess of 2,3-dimethyl-1,3-butadiene was added to a solution of **4a** (150 mg, 4.80 mmol) in dry chloroform (5 ml) and the mixture was stirred in dark at room temperature until the yellow color had been disappeared after 2 weeks. After the removal of the solvent under reduced pressure, colorless oil of **5a** as a mixture of two diasteriomers was formed, in 72% yield.

Mixture of two isomers: ^1H NMR ($CDCl_3$-d_6) ppm: 1.64 (s, 6H), 2.08 (d, 1H, $J = 3.2$ Hz), 2.13 (d, 1H, $J = 2.4$ Hz), 3.53 (d, 1H, $J = 17.2$ Hz), 3.63 (d, 1H, $J = 16$ Hz), 7.29–7.40 (m, 10H), 7.51–7.66 (m, 8H); ^{13}C NMR ($CDCl_3$-d_6) ppm: 19.17, 19.22, 19.33, 19.46, 36.55, 37.25, 52.27, 52.53, 75.01, 76.25, 117.69, 118.12, 124.72, 128.25, 128.42, 128.48, 128.60, 128.68, 128.83, 128.91, 128.95, 128.99, 129.80, 129.94, 135.34, 136.49,

136.84, 137.63, 138.13, 138.92; Anal. Calcd for: $C_{19}H_{19}ClOS_3$ (394.5): C, 57.79; H, 4.82; S, 24.33 Found: C, 58.06; H, 4.65; S, 24.46%.

5,6-Dihydro-3,4-dimethyl-6-(*p*-chlorophenylthio)-6(pentachlorophenylthio)-2H-thiopyran-*S*-oxide 5b

A large excess of 2,3-dimethyl-1,3-butadiene was added to a solution of **4b** (200 mg, 4.10 mmol) in dry chloroform (5 ml) and the mixture was stirred in dark at room temperature until the yellow color had had disappeared after 2 weeks. After the removal of the solvent under a reduced pressure, an oily substance was formed, which upon treating with petroleum ether and cooling it gave a solid residue which was recrystallized from chloroform/ether (1:3), in 77% yield as a colorless crystals of **5b** as a mixture of two diasteriomers; m.p. 59–61°C.

Mixture of two isomers: ^{1}H NMR ($CDCl_3$-d_6) ppm: 1.63 (s, 3H), 1.66 (s, 3H), 1.88 (s, 3H), 1.93 (s, 3H), 2.44 (d, 1H, $J = 16$ Hz), 2.61 (d, 1H, $J =$ 18.4 Hz), 2.93 (d, 1H, $J = 16$ Hz), 2.61 (d, 1H, $J = 18.4$ Hz), 2.93 (d, 1H, $J = 16$ Hz), 3.26 (d, 1H, $J = 19.2$ Hz), 3.53 (d, 1H, $J = 17.2$ Hz), 3.78 (d, 1H, $J = 16$ Hz), 4.12 (d, 1H, $J = 16$ Hz), 7.54 (d, 2H, $J = 8.4$ Hz), 7.58 (d, 2H, $J = 12$ Hz), 7.80 (d, 2H, $J = 8.4$ Hz), 7.83 (d, 2H, $J = 12.2$ Hz); ^{13}C NMR ($CDCl_3$-d_6) ppm: 17.95, 19.27, 19.39, 19.96, 24.52, 35.29, 36.29, 52.45, 52.71, 65.32, 79.09, 79.82, 116.72, 118.89, 124.59, 124.84, 125.79, 128.86, 128.99, 129.44, 130.45, 131.67, 132.02, 132.30, 136.46, 136.89, 137.86, 139.03, 140.47, 141.30; MS m/z (%) 564 (4, M, $C_{19}H_{14}Cl_6OS_3$, 421 (2, $C_{13}H_{10}Cl_5OS_2$), 281 (23, $C_{13}H_{10}ClOS_2$), 266 (100, $C_{12}H_7ClOS_2$), 247 (55, C_6Cl_5), 143 (85, $C_6H_4Cl_5$); Anal. Calcd. for $C_{19}H_{14}Cl_6OS_3$ (567): C, 40.21; H, 2.47; S, 16.93 Found: C, 40.60; H, 2.64; S, 16.91%.

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